ELSEVIER

Chemistry and Physics of Lipids
82 (1996) 33–37

CPL
CHEMISTRY AND PHYSICS OF LIPIDS

Evaluation of the olefinic proton signals in the ^{1}H-NMR spectra of allylic hydroxy groups in long-chain compounds

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Received 26 February 1996; accepted 8 April 1996

Abstract

The positional isomers of monounsaturated long-chain fatty compounds containing allylic hydroxy groups (shown for *trans* double bonds) are distinguished by ^{1}H-NMR spectroscopy through the chemical shift differences of the olefinic protons. These differences are expressed as rational functions (the differences being proportional to the negative third power of the position of the unsaturation), or logarithmic functions (the differences being proprtional to the position of the unsaturation raised as power). The present results on more sensitive ^{1}H-NMR spectra complement previous work on the ^{13}C-NMR spectra of these compounds. Theoretical models for explaining shifts in ^{13}C-NMR therefore also apply to ^{1}H-NMR.

Keywords: ^{1}H-NMR spectroscopy; Rational functions; Logarithmic functions; Allylic hydroxy groups; Fatty acids; Fatty esters

1. Introduction

Recently, we evaluated the ^{13}C-NMR signals of the olefinic carbons of various unsaturated fatty compounds [1,2]. The shift values of the individual carbons as well as the separations in the shifts of the olefinic carbons were shown to be rational functions. The equations for the shifts of olefinic carbons in fatty acids and esters with allylic hydroxy groups (*trans* double bonds) were proportional to the negative third power of the position of the unsaturation (denoted u) in the chain. The diastereomers of fatty compounds with allylic dihydroxy groups (2(*E*)-ene-1,4-diols) can be distinguished by both ^{1}H-NMR and ^{13}C-NMR spectroscopy [3]. The positional isomers of fatty compounds with allylic hydroxy groups (2(*E*)-1-

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PII S0009-3084(96)02559-5

ols) were discernible by ^{13}C-NMR spectroscopy [3]. The multitude of effects on the shifts of both protons and carbon atoms in NMR mentioned above led us to search for a method of distinguishing the positional isomers of the allylic monohydroxy compounds by ^{1}H-NMR spectroscopy. We now review in detail the ^{1}H-NMR spectra of the fatty compounds with allylic hydroxy groups synthesized previously [3–6] and evaluate the signals of the olefinic protons in a fashion similar to the carbons [1]. The results are reported here.

2. Results and discussion

2.1. Definitions

The allylic hydroxy compound with the hydroxy group closer to C1 will be called the position I compound, while its congener with the hydroxy group farther from C1 will be termed the position II compound [4]. The structures are depicted in Fig. 1.

In ^{13}C-NMR spectra, we reported [1] that the shifts and their separations of olefinic carbons in fatty compounds with allylic hydroxy groups can

Fig. 1. Position I and position II allylic hydroxy compounds (R′ = $(CH_2)_xCH_3$ and R′ = $(CH_2)_xCO_2H$ or $(CH_2)_xCO_2CH_3$).

be evaluated as rational functions. The separation s (in ppm) of the olefinic carbon signals was defined as

$$s = R_2 - R_1 \quad (1)$$

in which R_1 and R_2 are the individual carbon signals. Mathematically, the separations were expressed by rational functions with the general formula

$$s = (a/u^b) \pm f \quad (2)$$

in which u is the position of the unsaturation, a and f are parameters determined from individual plots, and b is the empirically determined power of u.

Fig. 2 depicts the ^{1}H-NMR signals of the two protons. For evaluation, the median shift value (in ppm) of the signals of the two protons was used.

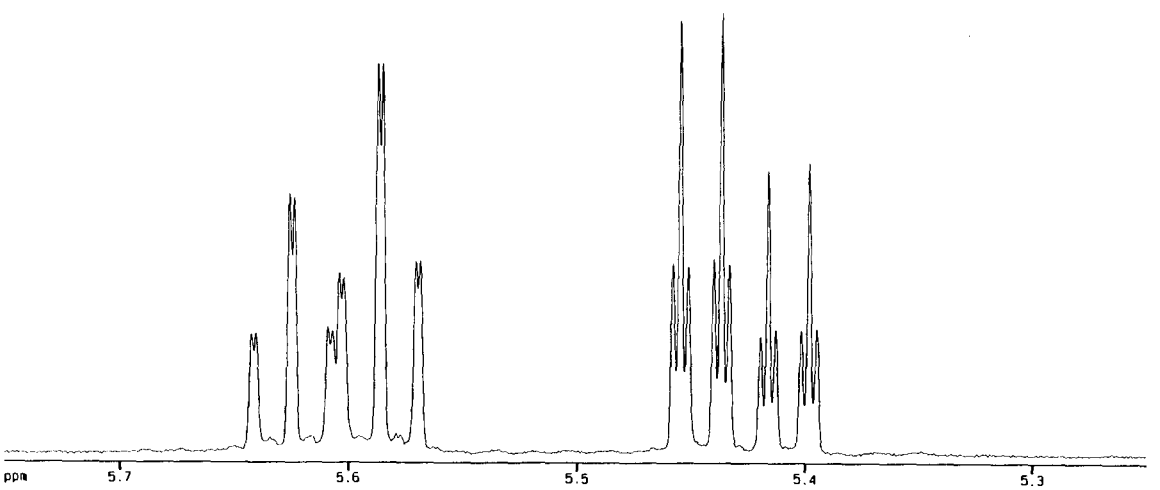

Fig. 2. Typical ^{1}H-NMR signals (δ scale) of the olefinic protons in long-chain compounds with an allylic hydroxy group. The upfield doublet of doublets is attributed to the olefinic proton adjacent to the hydroxy bearing carbon. The signals are split due to long-range coupling.

Table 1
Separation values s (in ppm) for position I and position II allylic hydroxy fatty compounds

u[a]	Functional group at C1				
	Acid		Ester		Alcohol[b]
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
Position I					
5	–		–		
6	–		–		0.193
7	0.199	0.200	0.195	0.194	
8	0.194	0.195	0.190	0.191	–
9	0.193	0.192	0.190	0.189	0.188
10	0.191	0.190	0.187	0.188	
11	0.190	0.189	0.187	0.187	0.185 (0.183)
12	–		–		–
13	0.189	0.187	0.186	0.186	
Position II					
5	0.117	0.118	0.119	0.122	–
6	0.153	0.148	0.154	0.151	0.167
7	0.162	0.164	0.167	0.165	
8	0.171	0.172	0.173	0.174	
9	0.180	0.178	0.176	0.178	0.181
10	0.181	0.181	0.180	0.181	–
11	0.185	0.183	0.183	0.184	0.181 (0.184)
12	–		–		–
13	0.188	0.186	0.185	0.186	

All observed values were obtained from spectra of compounds synthesized previously [3–5]. The observed values of the acids are plotted in Fig. 3. Calculated values were obtained from Eqs. (3)–(6).
[a]u denotes the position of the unsaturation.
[b]Data for compounds with hydroxy groups at C1 which were synthesized in [1]. The data for these fatty alcohol-derived compounds were not evaluated due to sparseness of datapoints. It is highly likely that evaluation would yield results similar to those for acids and esters. The values in parentheses result from compounds with different chain lengths but unsaturation at the same position [3].

We found that the separations (calculated for the median shift values) of the olefinic protons when determined to 10^{-3} ppm (instead of rounding to the usual 10^{-1} or 10^{-2} ppm) of the olefinic protons can be used to distinguish the positional isomers of the allylic hydroxy compounds. The separations of the olefinic proton signals decrease with increasing distance between the double bond and the functional group at C1. Also, the shift separations of the position I allylic compounds are greater than those of the corresponding position II compounds.

Table 1 contains the shift separations for the present compounds. All the values in this table for acids and esters were derived from ^{1}H-NMR spectra obtained from previously synthesizes compounds [3–6]. Fig. 3 depicts the values given in Table 1 for acids. The values converge to shift separation of 0.185 to 0.190 ppm for Δ 13 unsaturation depending on the functional group at C1. The allylic monohydroxylation products of symmetrical alkenes [6] show corresponding separations of their olefinic protons in ^{1}H-NMR. For example, the shift separation of the olefinic protons in 9(E)-octadecen-8-ol [6] is 0.187 ppm.

In analogy to the method presented previously [1], we determined rational functions of the kind given in Eq. (2) which approximately the observed values. For position I fatty acids, the equation

$$s = (5/u^3) + 0.185 \quad (3)$$

gives a good approximation. For methyl esters a slight modification of Eq. (1).

$$s = (3/u^3) + 0.185 \quad (4)$$

agrees well with experimental data.

Position II fatty acids are approximated by

$$s = (-9/u^3) + 0.19 \quad (5)$$

and for the corresponding methyl esters we obtain

$$s = (-8.5/u^3) + 0.19 \quad (6)$$

Note that there are slight deviations between the fatty acids and esters, an observation that is attributed to the differences in the functional groups [4].

The separations are proportional to the negative third power of the position of the unsaturation. Similar relationships were observed for the olefinic carbon signals of the same compounds [1].

The fact that the allylic hydroxy group is already several carbon atoms removed from the group at C1 influences the overall quality of the approximation. Nevertheless, the magnitude of the effect quantified here would presumably not change even with additional data. To the best of our knowledge, relationships as presented here were not derived previously for ^{1}H-NMR spectra.

Data for compounds with hydroxy groups at C1 (fatty alcohols; included in Table 1) were not evaluated because of their sparseness although it is likely that equations could be derived for more abundant data.

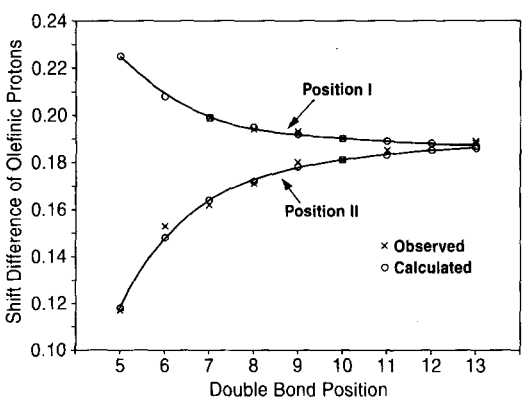

Fig. 3. Observed shift separations of olefinic protons in fatty acids with allylic hydroxy groups. Similar plots are possible for the corresponding fatty esters or compounds with hydroxy groups at C1.

The results of ^{13}C-NMR evaluation were discussed previously [1] in terms of the electric field model [7,8] for explaining the shifts of the unsaturated carbons. The Eqs. (3)–(6) are of the same nature as derived previously [1].

Recently, a model challenging the electric field model has been proposed ([9], personal communication from O.W. Howarth) which argues for through-bond, σ-inductive effects. With this model, different equations (logarithmic functions) are derived for the olefinic protons which are

$$s = 1.8^u + 0.188 \quad (7)$$

for acids with position I hydroxy groups and

$$s = -1.7^u + 0.188 \quad (8)$$

for acids with position II hydroxy groups. Generally, the quality of the approximation of the observed values by both methods is comparable.

Although the compounds studied here all possess *trans* double bond configuration, it is likely that similar equations hold for *cis* double bonds. This similarity was observed in the ^{13}C-NMR spectra of *cis*- and *trans*-octadecenoic acids [5]. Furthermore, the spectra of other unsaturated long-chain compounds (for example, unsubstituted alkenoic acids and esters) can probably be evaluated in a similar manner, but data on their ^{1}H-NMR spectra has not been reported. Obviously, excellent resolution of the olefinic protons would also be required because, when lacking a close functional group, the signals of the olefinic carbons will overlap considerably. Similar effects may also exist for alkynoic acids and esters.

It may be noted that, although the ^{1}H-NMR spectra discussed in this work were obtained earlier under routine, non-quantitative conditions, stringent quantitative replication of the results is possible (conditions described in the Experimental, Section 3). For this replication, a series of position II hydroxy acids with $\Delta 5$–$\Delta 11$ unsaturations was selected. The agreement in chemical shift differences with the routine spectra and calculated values was excellent. The differences were 0.116 ppm at $\Delta 5$, 0.15 ppm at $\Delta 6$, 0.161 at $\Delta 7$, 0.172 ppm at $\Delta 8$, 0.179 ppm at $\Delta 9$ 0.181 ppm at $\Delta 10$ and 0.183 ppm at $\Delta 11$.

In conclusion, it is possible to distinguish the positional isomers and the position of the double bond of allylic monohydroxy fatty compounds by ^{1}H-NMR. The tool for accomplishing this is the chemical shift difference of the olefinic protons. Equations (differing with the kind of model used to describe the effects) describing this phenomenon were derived. Therefore, theoretical models, previously only derived for the signals of unsaturated carbons in ^{13}C-NMR, apply to ^{1}H-NMR as well. The higher sensitivity of ^{1}H-NMR compared to ^{13}C-NMR allows the use of less sample to study such effects. Furthermore, the present and previous work [1,4–6] on the allylic hydroxy group shows that this group is nearly ideal for studying a multitude of effects in ^{13}C-NMR and ^{1}H-NMR spectra of long-chain compounds.

3. Experimental

All compounds used in this work were synthesized earlier by hydroxylation of monounsaturated fatty compounds with the selenium dioxide/*tert*-butylhydroperoxide system [3–6]. The routine, non-quantitative ^{1}H-NMR spectra discussed here were obtained from this work [3–6].

For quantitative replication, spectra were obtained of 10 mg sample (synthesized by the work discussed in [3–5]) dissolved in 0.45 ml $CDCl_3$ on a Bruker ARX-400 spectrometer operating at 400 MHz. The acquisition time was 10.87 s, sweep width 3012 Hz, data set Size was 64K, and the resolution was ± 0.1 Hz.

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